

# Central Waitemata Harbour Contaminant Study

Background Metal Concentrations in

Soils: Methods and Results

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Reviewed by:		Approved for ARC publication by:		
Metr.		Matthew Oanis		
Name:	Hayden Easton	Name: Matthew Davis		
Position:	Team Leader	Position: Group Manager		
	Stormwater Action Team	Partnerships & Community Programmes		
Organisation: Auckland Regional Council		Organisation: Auckland Regional Council		
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# Central Waitemata Harbour Contaminant Study. Background Metal Concentrations in Soils: Methods and Results

Jacquie Reed

#### Prepared for

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National Institute of Water & Atmospheric Research Ltd Gate 10, Silverdale Road, Hamilton P O Box 11115, Hamilton, New Zealand Phone: 07 856 7026 Fax: 07 856 0151 www.niwa.co.nz

## Preface

The Waitemata Harbour is comprised of tidal creeks, embayments and the central basin. The harbour receives sediment and stormwater chemical contaminant run-off from urban and rural land from a number of subcatchments, which can adversely affect the ecology. An earlier study examined long-term accumulation of sediment and stormwater chemical contaminants in the Upper Waitemata Harbour. However, previously little was known about the existing and long-term accumulation of sediment and stormwater chemical contaminants in the central harbour. The Central Waitemata Harbour Contaminant Study was commissioned to improve understanding of these issues. This study is part of the 10-year Stormwater Action Plan to increase knowledge and improve stormwater management outcomes in the region. The work was undertaken by the National Institute of Water and Atmospheric Research (NIWA).

The scope of the study entailed:

- 1) field investigation,
- development of a suite of computer models for
  - a. urban and rural catchment sediment and chemical contaminant loads,
  - b. harbour hydrodynamics and
  - c. harbour sediment and contaminant dispersion and accumulation,
- 3) application of the suite of computer models to project the likely fate of sediment, copper and zinc discharged into the central harbour over the 100-year period 2001 to 2100, and
- 4) conversion of the suite of computer models into a desktop tool that can be readily used to further assess the effects of different stormwater management interventions on sediment and stormwater chemical contaminant accumulation in the central harbour over the 100-year period.

The study is limited to assessment of long-term accumulation of sediment, copper and zinc in large-scale harbour depositional zones. The potential for adverse ecological effects from copper and zinc in the harbour sediments was assessed against sediment quality guidelines for chemical contaminants.

The study and tools developed address large-scale and long timeframes and consequently cannot be used to assess changes and impacts from small subcatchments or landuse developments, for example. Furthermore, the study does not assess ecological effects of discrete storm events or long-term chronic or sub-lethal ecological effects arising from the cocktail of urban contaminants and sediment.

The range of factors and contaminants influencing the ecology means that adverse ecological effects may occur at levels below contaminant guideline values for individual chemical contaminants (i.e., additive effects due to exposure to multiple contaminants may be occurring).

Existing data and data collected for the study were used to calibrate the individual computer models. The combined suite of models was calibrated against historic sedimentation and copper and zinc accumulation rates, derived from sediment cores collected from the harbour.

Four scenarios were modelled: a baseline scenario and three general stormwater management intervention scenarios.

The baseline scenario assumed current projections (at the time of the study) of

- future population growth,
- future landuse changes,
- expected changes in building roof materials,
- projected vehicle use, and
- existing stormwater treatment.

The three general stormwater management intervention scenarios evaluated were:

- 1) source control of zinc by painting existing unpainted and poorly painted galvanised steel industrial building roofs;
- 2) additional stormwater treatment, including:
  - o raingardens on roads carrying more than 20,000 vehicles per day and on paved industrial sites,
  - silt fences and hay bales for residential infill building sites and
  - pond / wetland trains treating twenty per cent of catchment area;
     and
- 3) combinations of the two previous scenarios.

#### International Peer Review Panel

The study was subject to internal officer and international peer review. The review was undertaken in stages during the study, which allowed incorporation of feedback and completion of a robust study. The review found:

- a state-of-the-art study on par with similar international studies,
- uncertainties that remain about the sediment and contaminant dynamics within tidal creeks / estuaries, and
- inherent uncertainties when projecting out 100 years.

#### Key Findings of the Study

Several key findings can be ascertained from the results and consideration of the study within the context of the wider Stormwater Action Plan aim to improve stormwater outcomes:

- Henderson Creek (which drains the largest subcatchment and with the largest urban area, as well as substantial areas of rural land) contributes the largest loads of sediment, copper and zinc to the Central Waitemata Harbour. The second largest loads come from the Upper Waitemata Harbour.
- Substantial proportions of the subcatchment sediment, copper and zinc loads are accumulating in the Henderson, Whau, Meola and Motions tidal creeks and in the Shoal Bay, Hobson Bay and Waterview embayments.
- Central Waitemata Harbour bed sediment concentrations of copper and zinc are not expected to reach toxic levels based on current assumptions of future trends in urban landuse and activities.
- Zinc source control targeting industrial building roofs produced limited reduction
  of zinc accumulation rates in the harbour because industrial areas cover only a
  small proportion of the catchment area and most unpainted galvanised steel
  roofs are expected to be replaced with other materials within the next 25 to 50
  years.
- Given that the modelling approach used large-scale depositional zones and long timeframes, differences can be expected from the modelling projections and stormwater management interventions contained within these reports versus consideration of smaller depositional areas and local interventions. (For example, whereas the study addresses the Whau River as a whole, differences exist within parts of the Whau River that may merit a different magnitude or type of intervention than may be inferred from considering the Whau River and its long-term contaminant trends as a whole.) As a consequence, these local situations may merit further investigation and assessment to determine the best manner in which to intervene and make improvements in the short and long terms.

#### Research and Investigation Questions

From consideration of the study and results, the following issues have been identified that require further research and investigation:

- Sediment and chemical contaminant dynamics within tidal creeks.
- The magnitude and particular locations of stormwater management interventions required to arrest sediment, copper and zinc accumulation in tidal creeks and embayments, including possible remediation / restoration opportunities.
- The fate of other contaminants derived from urban sources.
- The chronic / sub-lethal effects of marine animal exposure to the cocktail of urban contaminants and other stressors such sediment deposition, changing sediment particle size distribution and elevated suspended sediment loads.
- Ecosystem health and connectivity issues between tidal creeks and the central basin of the harbour, and the wider Hauraki Gulf.

#### Technical reports

The study has produced a series of technical reports:

#### Technical Report TR2008/032

Central Waitemata Harbour Contaminant Study. Landuse Scenarios.

#### Technical Report TR2008/033

Central Waitemata Harbour Contaminant Study. Background Metal Concentrations in Soils: Methods and Results.

#### Technical Report TR2008/034

Central Waitemata Harbour Contaminant Study. Harbour Sediments.

#### Technical Report TR2008/035

Central Waitemata Harbour Contaminant Study. Trace Metal Concentrations in Harbour Sediments.

#### Technical Report TR2008/036

Central Waitemata Harbour Contaminant Study. Hydrodynamics and Sediment Transport Fieldwork.

#### Technical Report TR2008/037

Central Waitemata Harbour Contaminant Study. Harbour Hydrodynamics, Wave and Sediment Transport Model Implementation and Calibration.

#### Technical Report TR2008/038

Central Waitemata Harbour Contaminant Study. Development of the Contaminant Load Model.

#### Technical Report TR2008/039

Central Waitemata Harbour Contaminant Study. Predictions of Stormwater Contaminant Loads.

#### Technical Report TR2008/040

Central Waitemata Harbour Contaminant Study. GLEAMS Model Structure, Setup and Data Requirements.

#### Technical Report TR2008/041

Central Waitemata Harbour Contaminant Study. GLEAMS Model Results for Rural and Earthworks Sediment Loads.

#### Technical Report TR2008/042

Central Waitemata Harbour Contaminant Study. USC-3 Model Description, Implementation and Calibration.

#### Technical Report TR2008/043

Central Waitemata Harbour Contaminant Study. Predictions of Sediment, Zinc and Copper Accumulation under Future Development Scenario 1.

#### Technical Report TR2008/044

Central Waitemata Harbour Contaminant Study. Predictions of Sediment, Zinc and Copper Accumulation under Future Development Scenarios 2, 3 and 4.

#### Technical Report TR2009/109

Central Waitemata Harbour Contaminant Study. Rainfall Analysis.

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Michael Ahrens, NIWA

Willia Ferenz

Reviewed by:

Malcolm Green, NIWA

Approved for release by:

## Executive Summary

The overall aim of the Central Waitemata Harbour (CWH) Contaminant Study is to model contaminant accumulation (sediment, zinc, copper) within the harbour for the purposes of, amongst other things, identifying significant contaminant sources, and testing efficacy of stormwater treatment and industrial roof contaminant source control. The objective is to predict (using models) contaminant build up and movement in the CWH.

This report provides information on background concentrations of total recoverable concentrations of zinc and copper in soil samples from volcanic fields in Auckland City. The introduction of volcanic soils into receiving environments represents a "natural" or "background" input of trace metals compared to anthropogenic sources. In predicting accumulation of metals in receiving environments it is necessary to account for both natural and anthropogenic sources. Previous measurements of inorganic elements in soils (ARC, 2001) provide data on whole-soil samples in the Auckland region. This study expands on previous information by measuring metal concentrations on different particle size fractions of soils.

Sampling sites were selected where volcanic soils were relatively undisturbed since their formation. The majority of these sites were in public parks, reserves and domain areas, located away from urban sources of metal contamination. Sediment cores were homogenized to make one composite and wet sieved to <25  $\mu$ m, 25–63  $\mu$ m, 63–250  $\mu$ m and >250  $\mu$ m. The three smallest size classes were analysed for total zinc and total copper.

For total zinc, the interquartile ranges of concentrations determined at all sites were  $47-129 \text{ mg kg}^{-1}$  ( $<25 \mu\text{m}$ ),  $46-127 \text{ mg kg}^{-1}$  ( $25-63 \mu\text{m}$ ), and  $32-85 \text{ mg kg}^{-1}$  ( $63-250 \mu\text{m}$ ).

For total copper, the interquartile ranges of concentrations determined at all sites were 11–52 mg kg<sup>-1</sup> ( $<25 \mu m$ ), 10–49 mg kg<sup>-1</sup> (25–63  $\mu m$ ) and 7–39 mg kg<sup>-1</sup> (63–250  $\mu m$ ).

To guide the application of the Urban Stormwater Contaminant model (USC-3), which requires estimates of background metal concentrations, the results have been assembled by sub-catchments and corresponding stormwater outfalls.

### Introduction

Modelling and empirical data indicate that stormwater contaminants are rapidly accumulating in the highly urbanised side branches of the Central Waitemata Harbour (CWH). However, there is no clear understanding of the fate of contaminants exported from these side-branches into the main body of the harbour, or that of contaminants discharged directly into the harbour. This information is needed to ensure sustainability within the CWH.

In response to this need, the Auckland Regional Council contracted NIWA to conduct the Central Waitemata Harbour Contaminant Study. The study began in September 2005 and is scheduled to run for three years. The main aim of the study is to model contaminant (zinc, copper) and sediment accumulation within the CWH for the purposes of, amongst other things, identifying significant contaminant sources, and testing efficacy of stormwater treatment and industrial roof contaminant source control.

### 2.1 Study aims

The study aims to:

- predict contaminant loads based on past, present and future land use and population growth for each sub-catchment discharging into the CWH, allowing for stormwater treatment and industrial roof contaminant source control:
- predict dispersal and accumulation (or loss) of sediment and stormwater contaminants in the CWH;
- · calibrate and validate the dispersal/accumulation model;
- apply the various models to predict catchment contaminant loads and accumulation of copper, zinc and sediment in the CWH under specific scenarios that depict various combinations of projected land use/population growth, stormwater treatment efficiency, and industrial roof contaminant source control;
- determine from the model predictions the relative contributions of sediment and contaminant from individual sub-catchments and local authorities;
- provide an assessment of the environmental consequences of model outputs;
- provide technical reports on each component of the work; and
- provide a desktop application suitable.

#### 2.2 Model suite

The study centres on the application of three models that are linked to each other in a single suite:

- The GLEAMS sediment-generation model, which predicts sediment erosion from the land and transport down the stream channel network. Predictions of sediment supply are necessary because, ultimately, sediment eroded from the land dilutes the concentration of contaminants in the bed sediments of the harbour, making them less harmful to biota1.
- The CLM contaminant/sediment-generation model, which predicts sediment and contaminant concentrations (including zinc, copper) in stormwater at a point source, in urban streams, or at end-of-pipe where stormwater discharges into the receiving environment.
- The USC (Urban Stormwater Contaminant) contaminant/sediment accumulation model, which predicts sedimentation and accumulation of contaminants (including zinc, copper) in the bed sediments of the estuary. Underlying the USC model is yet another model: an estuarine sediment-transport model, which simulates the dispersal of contaminants/sediments by physical processes such as tidal currents and waves.

### 2.3 Work plan

There are eight modules in the work plan:

- Module 1 Implementation of the sediment-generation model.
- Module 2 Implementation of the contaminant/sediment-generation model.
- Module 3 Implementation of the contaminant/sediment-accumulation model.
- Module 4 Calibration and validation of the model suite.
- Module 5 Depiction of development scenarios, including stormwater treatment and industrial roof contaminant source control, as required.
- Module 6 Execution of the model suite to produce predictions of contaminant build-up in bed sediments of the CWH.
- Module 7 Evaluation of predictions with management.

This may lead to reconsideration of Module 5, and subsequent re-running of Module 6 until an acceptable development scenario can be found.

• Module 8 - Development of desktop application.

<sup>&</sup>lt;sup>1</sup> We use the term "contaminant" herein to mean chemical contaminants such as zinc and copper, and we refer to "sediments" separately.

### 2.4 This report

This report provides information on total recoverable concentrations of zinc and copper in soil samples from volcanic fields located in selected catchments adjacent to the Central Waitemata Harbour. These trace metals originate in surface soils from localised geological and soil-forming processes. Soils can be mobilised through natural processes (eg, erosion in storm events, weathering) and/or disturbances during land development (eg, urbanisation). The introduction of volcanic soils into receiving environments represents a "natural" or "background" input of trace metals compared to anthropogenic sources. In predicting accumulation of metals in receiving environments it is necessary to account for both natural and anthropogenic sources.

Previous measurements of inorganic elements in soils (ARC, 2001) provide data on whole-soil samples in the Auckland region. This report, which shows metal concentrations on the different particle size fractions that constitute the whole soil, adds to that information.

Soils have been fractionated into four class sizes: <25  $\mu$ m, 25–63  $\mu$ m, 63–250  $\mu$ m and >250  $\mu$ m. Analyses have been conducted on the three smallest size classes only.

The methods used to collect and fractionate soils and to analyse the fractions are reported herein

The metal loads to be used in the USC-3 model will account for the background metals that are associated with natural soils in the Auckland region, as reported herein.

### Methods

Soil sampling was carried out by NIWA in March 2007. Sites selected for sampling are known volcanic soils in parks surrounding the Central Waitemata Harbour (Figure 1).

Sites selected were based on previous experience from sampling in 2001 (ARC, 2001). Figure 2 shows the distribution of volcanoes and volcanic fields in the Auckland region (Kermode, 1992).

Figure 3 shows the sub-catchments of the Central Waitemata Harbour that have been defined for applying the USC-3 model. Note that some sub-catchments were not sampled because they do not have volcanic soils (for example, Westmere, Henderson Creek, Hobsonville, Little Shoal Bay and Shoal Bay East). These sub-catchments were investigated in another study (TIMPERLEY et al., 2008).

In the remaining sub-catchments, only one volcanic field existed and so only one site was sampled, except for the following sub-catchments:

- Motions Creek sub-catchment had two volcanic cones so two sites were sampled.
- Oakley Creek sub-catchment had three volcanic cones so three sites were sampled.
- Hobson's Bay sub-catchment had a number of small volcanic hotspots so several sites were sampled (n=9).
- Stanley Street and Cook Street sub-catchments had one volcanic field shared between them so only one site was sampled.
- Whau River sub-catchment had several parks with soils considered to be volcanic. This
  sub-catchment also had one reserve and a golf course close to the Whau Creek; the
  ARC requested soils be sampled from these sites and included in this study due to a
  lack of knowledge of these areas. The latter two sites are representative of disturbed
  soils and are not considered as background.

Results of the soil-sampling programme will be presented herein by the sub-catchments shown in Figure 3.

**Figure 1**Location of volcanic soils sampled in March 2007 for metal analysis. These sites were selected for the purposes of the Central Waitemata Harbour Study.

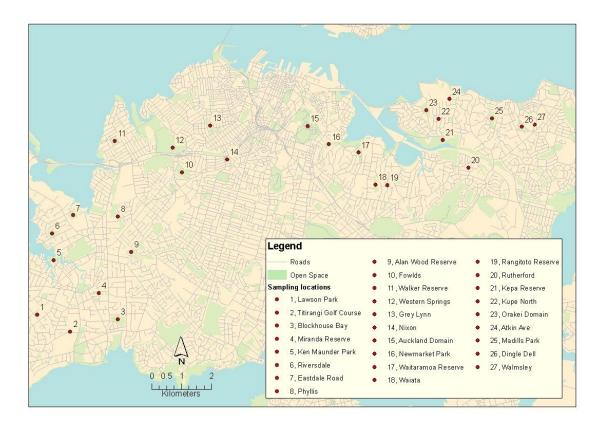
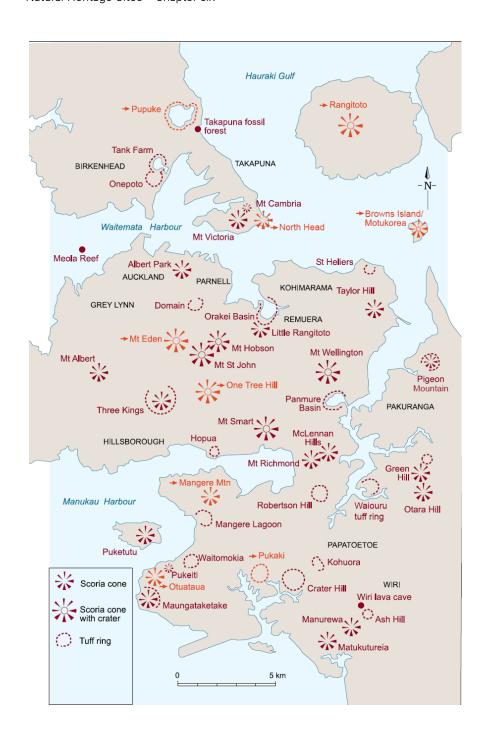


Figure 2

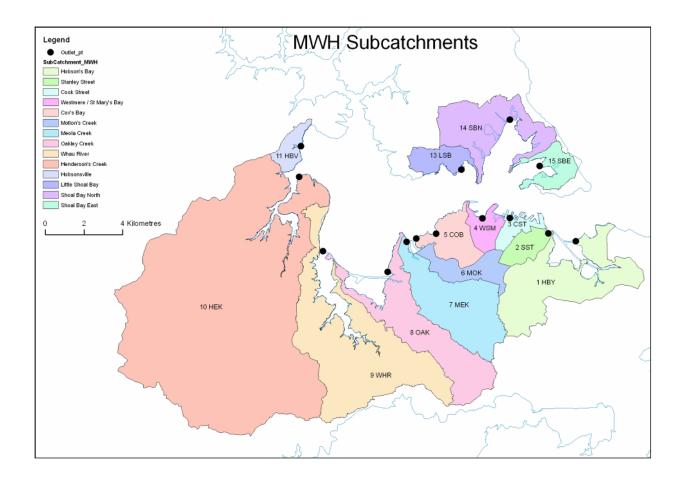
Map of Auckland's Volcanic Fields showing the 48 volcanoes (adapted from Crown Copyright:

Department of Conservation Our World Heritage: A Tentative List of New Zealand Cultural and

Natural Heritage Sites – Chapter six



**Figure 3**Sub-catchments and corresponding stormwater outfalls defined for the USC-3 model.

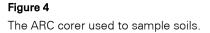


### 3.1 Sampling soils

The process of selecting the sites was similar to that used in a previous study (ARC, 2001). Primarily, sites were selected where volcanic soils were relatively undisturbed since their formation. The majority of these sites were in public parks, reserves and domain areas, located away from urban sources of metal contamination. The sites were located on higher ground so that soil erosion, creep, etc. would not influence natural metal concentrations.

At each sampling site (see Figure 1), a soil core of 150 mm length was taken using the ARC corer (Figure 4) at each of four random locations within 1 m of the designated location. The depth of core was chosen to represent the undisturbed soil layer (Timperley, M., pers. comm.). Cores were wrapped in foil and transported back to the NIWA laboratory.

Each core was homogenized to make one composite sample which was subsequently wet sieved to <25  $\mu$ m, 25–63  $\mu$ m, 63–250  $\mu$ m and >250  $\mu$ m. Each fraction was dried at 60°C to a constant weight. The dried fractions were lightly ground, weighed and the three smallest size classes were analysed for total zinc and total copper. The largest size class was kept in storage.





### 3.2 Analytical methodology

A 1 g sample of each dried soil was placed in a 50 mL polypropylene centrifuge tube and digested for 30 minutes at 95 °C in nitric/hydrochloric acid (2 mL HNO<sub>3</sub>, 2mL HCl, 10 mL water). Samples were diluted 10x with 1 per cent nitric acid prior to analysis to reduce acid strength and centrifuged at 2500 rpm for 10 minutes to remove suspended solids. The extracts were decanted into clean plastic tubes and analysed by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) according to APHA method 3125B. Detection limits were 0.2 mg kg<sup>-1</sup> d/w for Cu and 0.4 mg kg<sup>-1</sup> d/w for Zn.

### 3.2.1 Quality control and assurance

Calculations were based on standard calibrations with acidic working standards prepared from commercially-available stock solutions. A quality assurance assessment of the calibrations was carried out by analysing quality control standards made up from appropriate metal salts. Quality assurance was undertaken by the Hills Laboratory, Hamilton.

## 4 Results

All results of the analyses are shown in Appendix 1; Table 3 presents total zinc and Table 4 presents total copper concentrations in the size fractions <25  $\mu$ m, 25–63  $\mu$ m and 63–250  $\mu$ m. Note that the total cores were homogenized and a composite sample analysed, hence the reported concentrations represent the entire core depth.

The median concentrations of total zinc and total copper by sub-catchment (Figure 3) are shown in Tables 1 and 2, respectively.

Median, 25<sup>th</sup>-percentile and 75<sup>th</sup>-percentile concentrations by sub-catchment (Figure 3) are shown in Figures 5 to 7 for total zinc and in Figure 8 to 10 for total copper. Where only one site was sampled, no percentile data are shown.

Table 1

Median concentrations of total zinc (mg/kgd/w) by sub-catchment (Figure 3).

Outfall	Location code	Sites sampled	Sub-catchment	<25 µm	25–63 μm	63–250 μm
1	HBY	9	Hobson's Bay	72.4	62.9	57.7
2	SST	1	Stanley Street	86.3	104	80.5
3	CST	1	Cook Street	86.3	104	80.5
4	WSM	1 (Nixon)	Westmere/St Mary's Bay	106.0	91.9	66.9
5	СОВ	1	Cox's Bay	87.2	81.3	37.2
6	MOK	2	Motions Creek	121	115	78.9
7	MEK	1	Meola Creek	47.3	39.7	28.9
8	OAK	3	Oakley Creek	72.6	79	39.5
9	WHR	7	Whau River	61.1	46.5	34.9
10	HEK	NS	Henderson Creek	-	-	_
11	HBV	NS	Hobsonville	-	_	_
12	UWH	NS	Upper Waitemata Harbour	_	-	_
13	LSB	NS	Little Shoal Bay	-	_	_
14	SBN	1	Shoal Bay North	47.3	39.7	28.9
15	SBE	NS	Shoal Bay East	-	_	_

NS = Not sampled

Table 2

Median concentrations of total copper (mg/kg d/w) by sub-catchment (Figure 3).

Outfall	Location code	Sites sampled	Sub-catchment	<25 μm	25-63 μm	63-50 μm
1	HBY	9	Hobson's Bay	20	18	14.8
2	SST	1	Stanley Street	27.6	30.7	25.2
3	CST	1	Cook Street	27.6	30.7	25.2
4	WSM	1 (Nixon)	Westmere/St Mary's Bay	35.3	36.9	24.5
5	СОВ	1	Cox's Bay	26	24.9	12.9
6	MOK	2	Motions Creek	37.7	36.3	26.7
7	MEK	1	Meola Creek	10.9	9.8	7.4
8	OAK	3	Oakley Creek	44.1	40.4	28.3
9	WHR	7	Whau River	22.9	17.9	12.6
10	HEK	NS	Henderson Creek	-	_	-
11	HBV	NS	Hobsonville	-	_	-
12	UWH	NS	Upper Waitemata Harbour	_	-	_
13	LSB	NS	Little Shoal Bay	-	-	-
14	SBN	1	Shoal Bay North	10.9	9.8	7.4
15	SBE	NS	Shoal Bay East	_	-	-

NS = Not sampled

Figure 5 Median, 25-percentile and 75-percentile concentration of total zinc in soils sieved to <25  $\mu$ m, shown by sub-catchment (Figure 3).

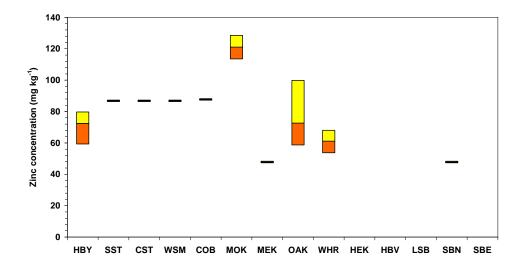


Figure 6 Median, 25-percentile and 75-percentile concentration of total zinc in soils sieved to 25–63  $\mu$ m, shown by sub-catchment (Figure 3).

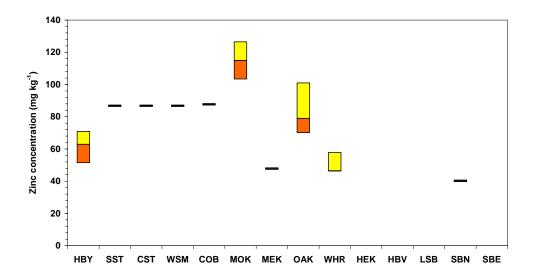


Figure 7 Median, 25-percentile and 75-percentile concentration of total zinc in soils sieved to 63–250  $\mu$ m, shown by sub-catchment (Figure 3).

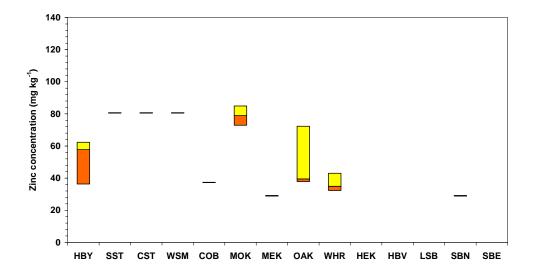


Figure 8 Median, 25-percentile and 75-percentile concentration of total copper in soils sieved to <25  $\mu$ m, shown by sub-catchment (Figure 3).

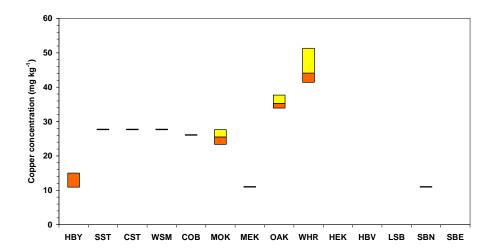


Figure 9 Median, 25-percentile and 75-percentile concentration of total copper in soils sieved to 25–63  $\mu$ m, shown by sub-catchment (Figure 3).

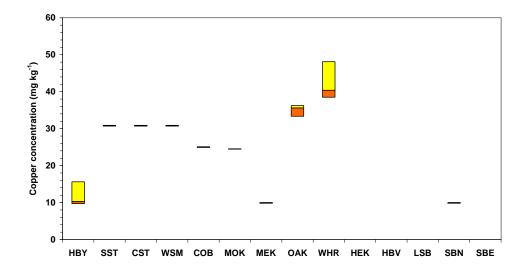
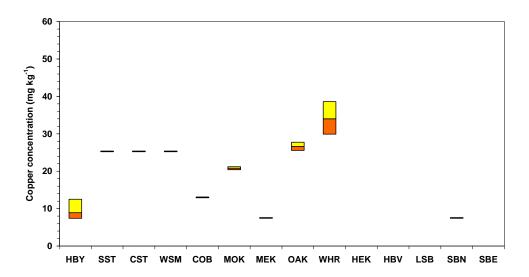


Figure 10 Median, 25°-percentile and 75°-percentile concentration of total copper in soils sieved to 63–250  $\mu$ m, shown by sub-catchment (Figure 3).



### Discussion

The interquartile ranges of metal concentrations in volcanic soils sampled in this study were:

#### **TOTAL ZINC**

47-129 mg kg<sup>-1</sup> for soil sieved at <25 μm

 $46-127 \text{ mg kg}^{-1}$  for soil sieved between  $25-63 \mu \text{m}$ 

 $32-85 \text{ mg kg}^{-1}$  for soil sieved between  $63-250 \mu m$ 

#### **TOTAL COPPER**

11–52 mg kg $^{-1}$  for soil sieved at <25  $\mu$ m

10–49 mg kg $^{-1}$  for soil sieved between 25–63  $\mu$ m

7-39 mg kg<sup>-1</sup> for soil sieved between 63-250 µm

If we combine these results, total metal concentrations in soils sampled at <250 µm were:

#### **TOTAL ZINC**

69-594 mg kg<sup>-1</sup>

#### **TOTAL COPPER**

21-192 mg kg<sup>-1</sup>

In a previous study (ARC, 2001), the median volcanic soil concentration for total zinc was 247 mg kg<sup>-1</sup>. For total copper it was 49 mg kg<sup>-1</sup>. Concentrations were found to vary widely, from 54.5–1160 mg kg<sup>-1</sup> for zinc, and 20.6–88.6 mg kg<sup>-1</sup> for copper. Results in ARC (2001) were based on sieving of soils to <2 mm. Soils in this study were sieved to <250  $\mu$ m, so a direct comparison with ARC (2001) results is not possible.

The zinc concentrations measured in this study are within the previously measured range for volcanic soils; however, at Kepa Reserve (in Hobson's Bay sub-catchment) total zinc concentration was approximately double this average at 594 mg kg<sup>-1</sup>. Although this seems high, it is within the expected range of zinc in volcanic soils (ARC, 2001). This site is included in the results for Hobson's Bay sub-catchment.

The copper concentrations measured in this study are within the expected range for volcanic soils; six sites have slightly higher concentrations outside this range  $\pm$  13 mg kg<sup>-1</sup>. Two sites fall beyond this range, located at Phyllis (138 mg kg<sup>-1</sup>) and Lawson (192 mg kg<sup>-1</sup>).

The two disturbed sites have particularly elevated total copper concentrations: Titirangi golf course (248 mg kg<sup>-1</sup>) and Riversdale Reserve in Avondale (571 mg kg<sup>-1</sup>). A possible reason is historical contamination through the use of horticultural products (eg, copper-based pesticides). These sites were not included in the analysis of results by subcatchment. Further research is required to establish the source of copper at these sites.

## Conclusions

We measured zinc and copper concentrations in volcanic soils surrounding the Central Waitemata Harbour. The results are reported by sub-catchment.

The range of total zinc concentration in soils sampled at <250  $\mu$ m was 69–594 mg kg<sup>-1</sup>. The range of total copper concentration in soils sampled at <250  $\mu$ m was 21–192 mg kg<sup>-1</sup>. The zinc and copper concentrations measured in this study are within the previously measured ranges for volcanic soils; however, the copper concentrations at two sites are higher than previously detected.

## 7 References

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# Appendix 1: Analytical Data

Table 3 Total zinc concentrations in all volcanic soils sampled in March, 2007, sieved to three size fractions and the total zinc concentrations (<250  $\mu$ m).

Location	Total recoverable zinc (<25 μm) (mg kg <sup>-1</sup> dw)	Total recoverable zinc (25–63 µm) (mg kg <sup>-1</sup> dw)	Total recoverable zinc (63—250 µm) (mg kg <sup>-1</sup> dw)	Sum of total recoverable zinc (<250 µm) (mg kg <sup>-1</sup> dw)
Atkin Ave	27.8	26.3	25.1	79
Miranda	28.2	23.9	16.4	69
Walker	44.8	79.0	36.2	160
Fowlds	47.3	39.7	28.9	116
Lawson Park	53.7	46.3	43.0	143
Waiata	54.3	51.5	36.3	142
Walmsley	54.6	44.6	37.4	137
Newmarket	59.3	67.3	29.6	156
Blockhouse Bay	61.1	46.5	32.3	140
Madills Park	65.8	48.6	39.7	154
Eastdale	68.0	63.2	56.7	188
Ken Maunder Park	68.2	57.8	34.9	161
Titirangi golf course	69.8	62.8	53.2	186
Orakei	71.6	70.9	62.3	205
Rutherford	72.4	49.5	61.8	184
Alan Wood	72.6	61.2	39.5	173
Kupe North	75.1	61.6	52.8	190
Waitaramoa Reserve	79.7	62.9	57.7	200
Auckland Domain	86.3	104	80.5	271
Grey Lyn	87.2	81.3	37.2	206
Dingle Dell	87.4	72.8	58.2	218
Nixon	106	91.9	66.9	265
Phyllis	127	123	105	355
Western Springs	136	138	90.9	365
Rangitoto Reserve	140	122	102	364
Riversdale	145	135	140	420
Kepa Reserve	238	188	168	594

**Table 4** Total copper concentrations in all volcanic soils sampled in March, 2007, sieved to three size fractions and the total copper concentrations (<250  $\mu$ m).

Location	Total recoverable copper (<25 µm) (mg kg <sup>-1</sup> dw)	Total recoverable copper (25–63 µm) (mg kg <sup>-1</sup> dw)	Total recoverable copper (63–250 µm) (mg kg <sup>-1</sup> dw)	Sum of total recoverable copper (<250 µm) (mg kg <sup>-1</sup> dw)
Atkin Ave	8.10	7.80	7.60	24
Miranda	8.70	7.40	5.00	21
Walker	21.2	24.6	20.0	66
Fowlds	10.9	9.80	7.40	28
Lawson Park	76.3	60.0	55.9	192
Waiata	16.2	15.6	12.5	44
Walmsley	13.0	11.9	10.2	35
Newmarket	15.0	13.7	8.90	38
Blockhouse Bay	22.9	17.9	12.6	53
Madills Park	22.4	16.6	13.4	52
Eastdale	32.5	31.1	26.6	90
Ken Maunder Park	11.4	10.3	6.20	28
Titirangi golf course	90.5	88.7	68.9	248
Orakei	20.4	20.5	18.6	60
Rutherford	15.5	9.70	11.6	37
Alan Wood	44.1	40.4	28.3	113
Kupe North	20.0	18.0	14.8	53
Waitaramoa Reserve	29.8	24.4	21.6	76
Auckland Domain	27.6	30.7	25.2	84
Grey Lyn	26.0	24.9	12.9	64
Dingle Dell	31.4	26.6	19.5	78
Nixon	35.3	36.9	24.5	97
Phyllis	51.3	48.1	38.6	138
Western Springs	40.1	35.6	28.9	105
Rangitoto Reserve	40.1	38.5	29.9	109
Riversdale	196	189	186	571
Kepa Reserve	41.4	37.9	34.0	113